Experimental EOS and Chemical Studies of High-Pressure Detonation Products and Product Mixtures

J.M. Zaug, L.E. Fried, J.C. Crowhurst, D.W. Hansen, W.M. Howard, G.S. Lee, P.F. Pagoria, E.H. Abramson

U.S. Department of Energy

Lawrence
Livermore
National
Laboratory

July 1, 2002

DISCLAIMER

EXPERIMENTAL EOS AND CHEMICAL STUDIES OF HIGH-PRESSURE DETONATION PRODUCTS AND PRODUCT MIXTURES *

Joseph M. Zaug, Lawrence E. Fried, Jonathan C. Crowhurst, Donald. W. Hansen,
W. Michael Howard, Gregory S. Lee, and Philip F. Pagoria
Lawrence Livermore National Laboratory
P.O. Box 808, Livermore, California 94551

Evan H. Abramson
Department of Chemistry
University of Washington,
Seattle, Washington, 98195

We present equation of state results from impulsively stimulated light scattering (ISLS) experiments conducted in diamond anvil cells on pure supercritical fluids, and supercritical fluid mixtures. We have made measurements on fluid H_2O (water), CH_2O (formaldehyde), and CH_3OH (methanol). Sound speeds measured through ISLS have allowed us to refine existing potential models used in the EXP6 detonation product library [Fried, L. E., and Howard, W. M., *J. Chem. Phys.* 109 (17): 7338-7348 (1998).]. The refined models allow us to more accurately assess the chemical composition at the Chapman-Jouget (C-J) state of common explosives. We predict that water and formaldehyde are present in appreciable quantities at the C-J state of HMX, RDX, and NM. Methanol is predicted to be present only in trace quantities at the C-J state. In the case of methanol, chemical decomposition and phase separation was observed at high temperatures. We are developing micro-FTIR and Raman techniques to determine the chemical composition of the phase separated detonation products.

INTRODUCTION

Experiments at extreme conditions of pressure and/or temperature provide insight into a realm of chemical and material properties that are significantly different from those encountered under ambient conditions. Such studies extend and test the theoretical framework which permits progress from properties at the atomic and molecular level to macroscopic behavior, constitute a potential source of novel materials and constitute a potential source of novel materials and new tools for chemical transformation and are important adjuncts to progress in other disciplines. There is no question that an improved general knowledge of electronic, physical, and chemical behavior of relevant constituent materials at high density is required, for example, for a less fragmented description of the processes that precede and direct detonation. The purpose of the work described in this paper is to ultimately develop a quantitative model of material properties and states under chemically and

physically extreme conditions not currently achievable in the laboratory setting.

Dynamical simulation based on approximate Born-Oppenheimer potentials plays a large and increasingly important role in chemistry and in the biological and materials sciences. More generally, knowledge of an effective interatomic potential function underlies any effort to predict or rationalize the properties of solids and liquids. Particularly in systems associated with experimentally difficult temperatures or pressures, such as those that prevail in detonations, the deep interiors of the Earth, and giant planets, models based on intermolecular potentials seems at present the most promising predictive resource. While there exists an extensive body of experimental techniques and experience on computational methods appropriate to ambient conditions, the regime of strong repulsive interactions at very high densities has not been as extensively investigated. The experiments discussed here are aimed both at enlarging the family of properties conveniently measured at high pressure and, principally, at providing the data appropriate to a critical test of the theory of the internuclear potential in simple substances at high density.

EXPERIMENTAL

The optical technique Impulsive Stimulated Light Scattering (ISLS) is discussed in general in Refs. [1-2] and specifically in the context of the DAC in Refs. [3-5]. Briefly, two successive "excitation" pulses, (30 μJ, 60 μm diameter, ~100 ps duration) are selected from the output train of a Q-switched (500 Hz), mode-locked Nd:YAG laser and recombined in the sample at an angle 2θ, but otherwise coincident in space and time. Interference

establishes a periodic distribution of intensity and, in a sample that absorbs in the near infrared, a (spatially) periodic variation in the temperature and pressure ensues. The coupling between laser light and the excited material modes is such that the local temperature rise remains "impulsive." The associated thermal pressure launches counter-propagating acoustic waves. The acoustic wavelength, d, in this case equal to the period of the optical grating, may be expressed in terms of the excitation wavelength, $\lambda_E = 1.064 \ \mu m$, and θ as

$$d = \lambda_A = \frac{\lambda_E}{2\sin\theta} \qquad (1)$$

In a fluid sample one longitudinal wave is excited. The impulsively excited acoustic wave induces a temporally and spatially periodic variation in the index of refraction of the sample. A third pulse (~1 μJ, 20 μm diameter, ~80 ps duration) selected from the same Q-switched envelope as the excitation pulses is frequency doubled ($\lambda_P = 0.532 \ \mu m$) and delayed by a combination of time of flight and mode lock pulse selection to generate the "probe." Observation of the intensity of the Bragg scattering of the probe, by the acoustic or thermoacoustic grating, as a function of probe delay serves to determine the frequency (ν), and hence the adiabatic velocity ($c = d\nu$) of the acoustic waves.

In practice, grating spacings are determined by making the same measurement on a piece of glass with a known speed of sound and which gives a strong, stable signal suitable for a calibrant. The glass was in turn calibrated against water and fused silica [6-8]. The velocity is typically determined with a precision of <±0.2%.

Pressure determinations were made by monitoring the wavelength of the fluorescence (excited by a He-Cd laser or by

the 488-nm Ar^+ laser line) of ruby chips which surround or are embedded in the sample. Rubies after grinding to tens of microns have residual strains which are often large enough to offset pressure measurements by ~0.05 GPa, and occasionally as much as 0.2 GPa. Annealing at ~1000·C for several hours decreases both the magnitude and frequency of these deviations yet it is still common to find rubies which differ reproducibly by the equivalent of 0.02 GPa. The most precise work completed has been on the melting curve of O_2, in which the relative wavelengths of rubies were recorded at 0 GPa and the high-pressure results corrected by the same amounts. The reference rubies at 1 atm were kept in the same temperature controlled housing as were the samples, because wavelength shifts equivalent to 0.01 GPa are generated by temperature differences of 0.5° C and in order to match as closely as possible the two spectral line shapes. With hydrostatic samples one can measure pressures with a precision of slightly better than 0.01 GPa. A 1/4m spectrometer (1200 grooves/mm grating) and 750 bin CCD (11 μm pixel width) gave a dispersion of 2.3×10^{-3} Å/bin. Micro FTIR spectra were taken using a Bruker Optics vector-33 FTIR spectrometer (4 cm^{-1} resolution). Micro Raman spectra were taken using a J-Y Labram system (2 cm^{-1} resolution).

Liquid formaldehyde is not available commercially, and exists only at low temperatures. Our chemical procedure was as follows: Into a dried 500 mL 3-necked round-bottomed flask fitted with a N_2 inlet and outlet, thermocouple, and surrounded by a heating mantle was placed approximately 80 g of paraformaldehyde (fills flask 2/3 full). The mixture was heated to decompose the paraformaldehyde with the internal temperature controlled with a

temperature controller set at 150 °C. The formaldehyde was initially collected (under a slow N_2 flow) in a small condensing trap cooled at CO_2/ acetone temperature to insure removal of residual water and any low boiling impurities. After about 5 mL of formaldehyde was collected in the trap the outlet tube was connected to the diamond anvil apparatus which was kept under a N_2 atmosphere and cooled to dry ice/ acetone temperatures. Enough formaldehyde was collected to completely cover the diamond anvil cell (~20 mL).

COMPUTATIONAL

CHEETAH is a thermochemical code that is used to predict detonation performance for solid and liquid explosives. CHEETAH solves thermodynamic equations between product species to find chemical equilibrium for a given pressure and temperature. Chapman-Jouget (C-J) theory says that the detonation point is a state in thermodynamic and chemical equilibrium, so CHEETAH can predict the properties of this state. From these properties and elementary detonation theory the detonation velocity and other performance indicators are computed.

Thermodynamic equilibrium is found by balancing chemical potentials, where the chemical potentials of condensed species are just functions of pressure and temperature, while the potentials of gaseous species also depend on concentrations. In order to solve for the chemical potentials, it is necessary to know the pressure-volume relations for species that are important products in detonation. Moreover, it is necessary to know these relations at the high pressures and temperatures that typically characterize the CJ state. Thus, there is a need for improved high-pressure equations of state for fluids, particularly for molecular fluid mixtures. The exponential-6 (EXP-6)

potential model defines the energy of interaction of a classical fluid composed of identical spherical particles. This model has been used with considerable success to describe the equation of state of many materials over a wide range of pressure and temperature [9].

The EXP-6 potential has also proved successful in modeling chemical equilibrium at the high pressures and temperatures characteristic of detonation. However, in order to calibrate the parameters for such models, it is necessary to have experimental data for molecules and mixtures of molecular species at high temperature and pressure. Static compression data, as well as sound speed measurements, provide important data for these models.

RESULTS AND DISCUSSIONS

The sound velocity of pure methanol (MeOH) was measured along a 250°C isotherm up to 3.9 GPa. After each data point was taken the sample was cooled and the velocity was again measured and compared to previous measurements of uncooked MeOH [10]. No appreciable velocity difference between data sets was observed. The measured sound speed for MeOH are given in Table I. A comparison of

ISLS experimental data and CHEETAH computational results are given in Figure 1. The EXP-6 potential model used was based on the shock Hugoniot of methanol. The ~3% difference between data sets shows the utility of CHEETAH and the consistency between static and dynamic equation of state measurements. The EXP-6 parameters for species considered here are given in Table II.
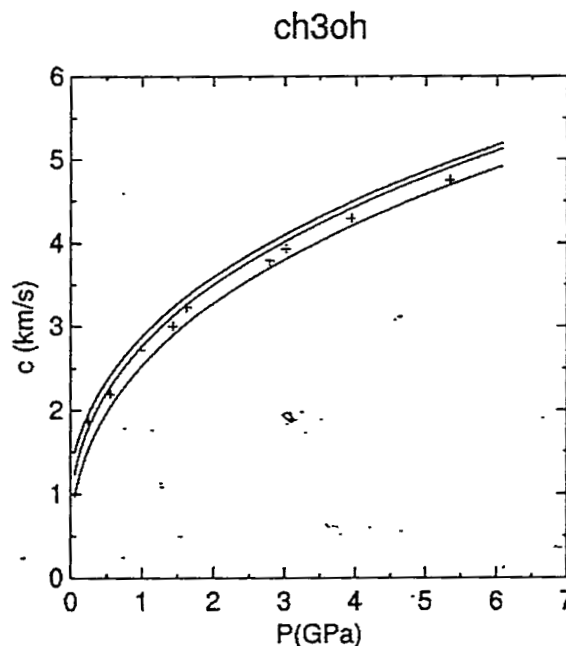
ch3oh

FIGURE 1: MEASURED SOUND SPEED FOR CH3OH AT 300°, 250°, AND 94°C (CROSSES) VERSUS CALCULATIONS.

TABLE 1. MEASURED VELOCITIES FOR CH3OH AT 250°C.

P(GPa)	c(km/s)
5.61	2.194
9.87	2.720
14.24	3.000
16.33	3.219
26.40	3.771
31.60	4.023
38.90	4.255

TABLE II: HEAT OF FORMATION (H0: KJ/MOL), STANDARD ENTROPY (S0: KJ/MOL-K), EXP-6 POTENTIAL MINIMUM (RM: A), WELL DEPTH (E: K) AND STEEPNESS PARAMETER (A) FOR SPECIES STUDIED IN THIS WORK.

| Species	H0	S0	rm	e	a
CH2O	-116	0.219	3.72	350	13.0
CH2Oa	-119	0.217	5.64	350	13.0
CH3OH	-201	0.240	4.24	507	13.0
H2O	-242	0.189	3.43	397	10.7
H2Oa	-288	0.093	3.21	397	10.7

An attempt was then made to measure the velocity of MeOH at 5 GPa, but at this pressure MeOH froze. The sample was then brought up to 325°C where it promptly began to phase separate into supercritical reaction products Figure 2. Upon cooling, brownish platelet looking forms were observed at 315°C. Some of the smaller bubbles contained diamond.


FIGURE 2: MEOH PRODUCT BUBBLES AT 232°C AND 5 GPa.

Heat was again applied, and the formation of carbon tendrils began at 331°C. These carbon tendrils retreated at 325°C. Upon cooling brown platelets re-appeared at 316°. At this point the furnace was removed from the optical table and placed on a microscope stage where digital micro-graphs were taken of the bubbles as they dissipated and eventually froze, Figure 3.
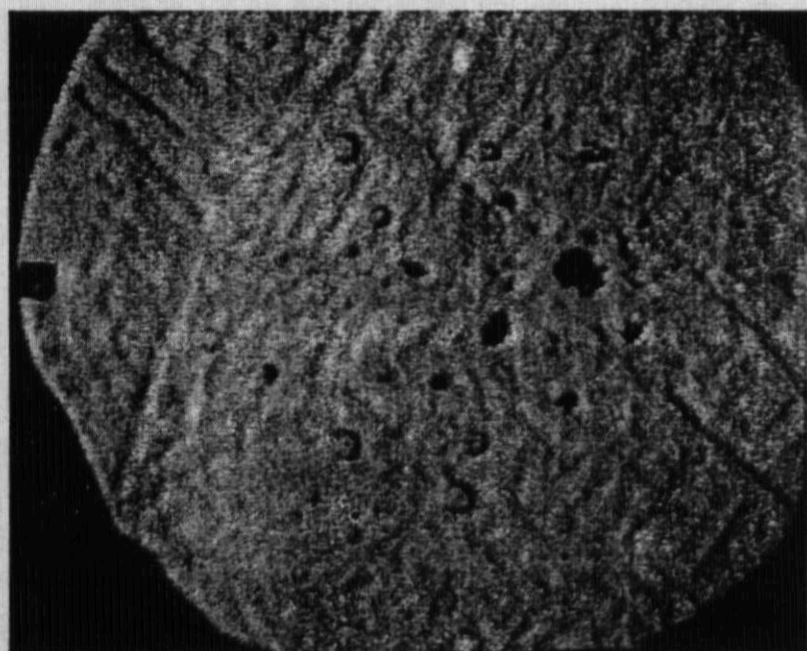
FIGURE 3: MEOH PRODUCTS FROZEN AT 32°C AND 5 GPa.

We compared FTIR spectra of the frozen sample to MeOH at ambient conditions. The results are shown in Figure. 4.
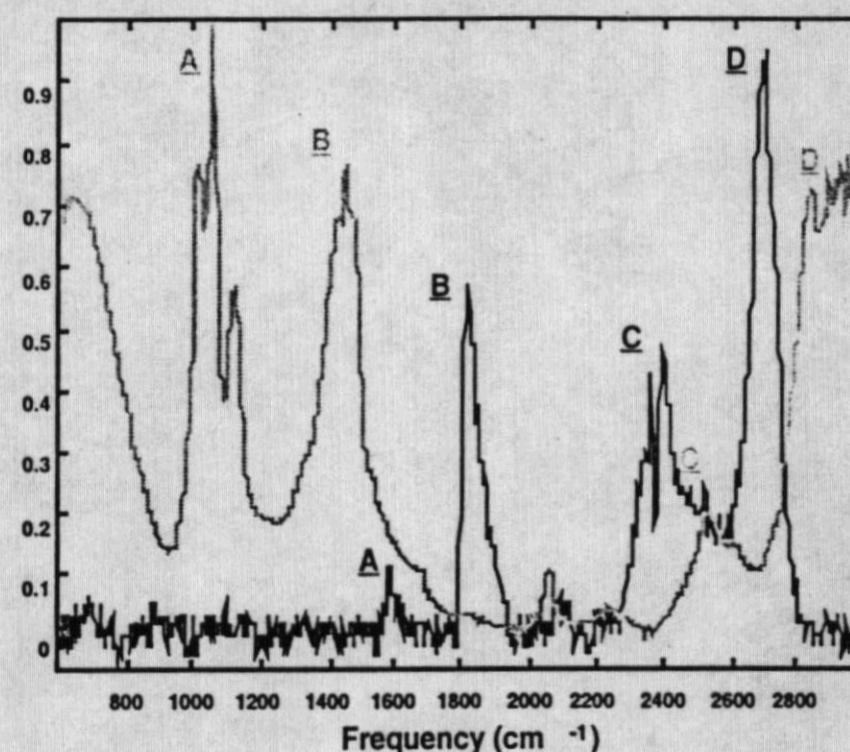
FIGURE 4: MICRO-FTIR SPECTRA OF PURE MEOH AT AMBIENT CONDITIONS (GRAY LINE) AND REACTED MEOH COOLED TO AMBIENT TEMPERATURE.

In addition FTIR spectra was taken of previously cooked MeOH (300°C) at 2.2 GPa and 24°C. The line assignments for ambient MeOH peaks A and B are C-O stretch and O-H bending + symmetrical CH_3 bending respectively. The C peaks are C-H stretching modes and peak D is O-H stretching with an intermolecular hydrogen bonded network.

High-pressure FTIR spectra indicate that pressure completely attenuates bending mode frequencies. The intensity of peak B (reacted MeOH spectra) increased with heat soak time above 300°C and may indicate the presence of a simple carbonyl, perhaps formaldehyde. Peak C is blue shifted C-H stretching modes and peak D is again O-H stretch where now there is no H-H exchange occurring.

ISLS measurements of the sound speed in CH2O were also performed. The same procedures were followed as for CH3OH.

The experimental results are given in Table III. CH2O is not in the current default product set for the CHEETAH library. Parameters were estimated using simple corresponding states theory. These gave results with an average absolute error of 42%. The CH2O parameters used with the JCZS product library were also compared to the experimental data. A 33% average absolute error was found. CH2O is a polar molecule. We have found that a two-species description of polar associated fluids can dramatically increase the accuracy of the EXP-6 model. In the present case, we use species CH2O and CH2Oa. CH2Oa is associated formaldehyde. CH2Oa has lower standard energy and entropy than CH2O. Parameters for CH2O and CH2Oa are given in Table II. A comparison between the two species model and the experimental data are given in Figure 5. Good agreement is seen, with an average error of 6%.

TABLE III: SOUND SPEED MEASUREMENTS FOR CH2O. REPEATED VALUES ARE BLANK.

P(GPa)	T(C)	C(km/s)
0.822	24	2.484
1.466	247	2.626
		2.608
		2.614
0.342	250	1.227
0.855		2.353
		2.332
2.023		3.072

Measurements were also performed on the sound speed of H2O. H2O is a known major detonation product, and is also a major component of several giant planetary atmospheres. Results are shown in Table IV.
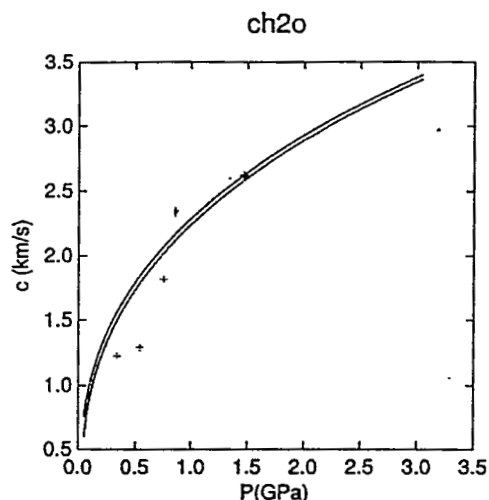
ch2o

FIGURE 5: MEASURED SOUND SPEED FOR CH2O AT 250° AND 300°C VS. CALCULATIONS.

TABLE IV: SOUND SPEED MEASUREMENTS OF H2O.

P(GPa)	T(C)	C(km/s)
0.86	100	2.612
1.105	100	2.788
1.410	100	3.028
1.600	100	3.161
2.150	100	3.471
1.00	115	2.734
1.44	115	3.065
1.65	115	3.182
2.19	115	3.465
2.29	115	3.516
0.88	150	2.631
2.314	150	3.541
0.500	200	2.254
0.937	200	2.685
1.090	200	2.800
2.770	200	3.706
3.060	200	3.823
3.230	200	3.885
3.590	200	4.020
1.621	300	3.059
2.195	300	3.372
3.612	300	3.951
4.513	300	4.246
5.206	300	4.424
5.543	300	4.517
1.120	400	2.660

1.130	400	2.660
1.417	400	2.844
2.179	400	3.304
2.605	400	3.500
3.513	400	3.857
3.675	400	3.923
4.689	400	4.234
4.893	400	4.310
4.903	400	4.310

The H2O sound speed data allowed us to refine the two species EXP-6 potential model used in CHEETAH. The refined potential model is given in Table II. The model is consistent with static sound speed and compression measurements, as well as shock Hugoniot pressures are temperatures. A comparison between the measured sound speed and the present two-species model is given in Figure 6.
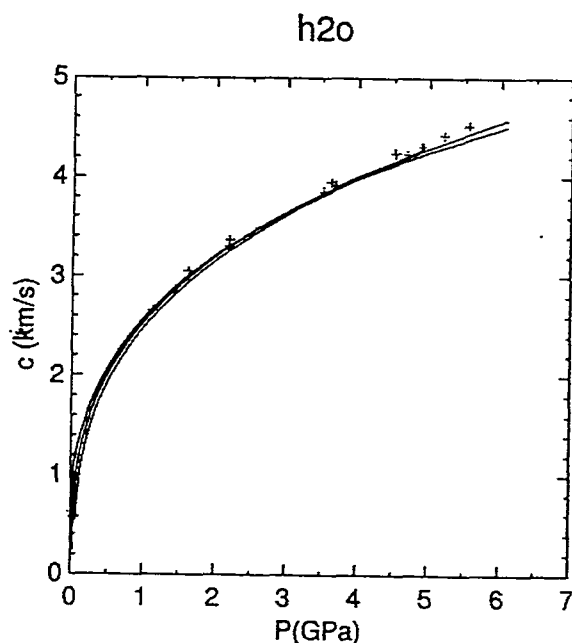
h2o

FIGURE 6: COMPARISON OF THE SOUND SPEED OF H2O AT 200°, 300°, AND 400°C WITH EXPERIMENTAL DATA.

·We have applied the present refinements to the EXP-6 product library used in CHEETAH. With the refined parameters, we can examine the nature of chemical

composition at Chapman-Jouget (CJ) detonation states. The CJ states of three common explosives, HMX, RDX, and NM, were determined with the CHEETAH program. Results are shown in Figure 7.
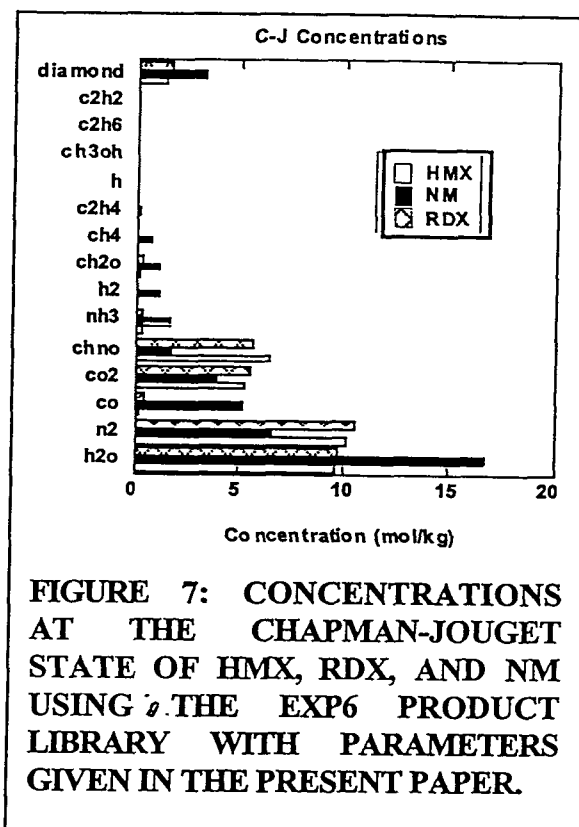
FIGURE 7: CONCENTRATIONS AT THE CHAPMAN-JOUGET STATE OF HMX, RDX, AND NM USING ɑ.THE EXP6 PRODUCT LIBRARY WITH PARAMETERS GIVEN IN THE PRESENT PAPER.

CONCLUSIONS

We have measured the sound speed of supercritical MeOH at 250°C up to 3.9 GPa. MeOH froze at 5 GPa. An attempt to carry on the sound speed study along a 325°C isotherm was thwarted by chemical reaction toward products that may include water, ethane, methane, diamond, and perhaps formaldehyde. We predict that CH2O is present in appreciable quantities in the C-J state of three prevalently used explosives. This is a somewhat surprising result. Successful thermochemical treatments of detonation have been developed either with or without CH2O. We compared the accuracy of detonation

7

velocities for a database of explosives containing C, H, N, and O. The inclusion of CH2O made little difference in the overall accuracy of the results. We also note that CH3OH is found in only trace quantities in our C-J calculations. This species may play a more important role in kinetic mechanisms of energetic material decomposition. Another interesting observation is that HNCO (isocyanic acid) is a major detonation product. The exp-6 model for this species is currently based on estimates used in the JCZS product library. Closer experimental investigation of the equation of state of this compound is called for. As expected, H2O was found to be a major detonation product. Further study of mixtures of H2O with other detonation products should enhance the accuracy of present-day thermochemical calculations.

VI. ACKNOWLEDGMENTS

REFERENCES

1. Yan, Y. X., Cheng L. T., and Nelson K. A., "Impulsive Stimulated Scattering," in Advances in Non-linear Spectroscopy, J. H. Clark and R. E. Hester, Eds. John Wiley Ltd. London, (1987).

2. Fayer, M. D., *IEEE J. Quantum Electronics*, 22, 1444, (1986).

3. Brown, J. M., Slutsky L. J., Nelson K. A., and Cheng L. T., "Velocity of Sound and Equation of State of Methanol and Ethanol in a Diamond Anvil Cell: An Application of Impulsive Stimulated Scattering," *Science*, 241, p. 65, (1988).

4. Zaug, J. M., Abramson, E. H., Brown, J. M. and Slutsky, L. J., "Elastic Constants, Equations of State and Thermal Diffusivity at High Pressure" in *High Pressure Research; Applications to Earth and Planetary Sciences*, Y. Syono and M. Manghnani Eds., 157-166, American Geophysical Union, Washington D. C., (1992).

5. Zaug, J. M., Ph.D. Thesis, (University of Washington, Seattle WA , December 1994).

6. Greenspan, M., and Tschiegg, C. E., *J. Acoust. Soc. Am.*, 31, 75-76, (1959).

7. Wilson W. D, *J. Acoust. Soc. Am.*, 31, 1067-1072, (1959).

8. American Institute of Physics Handbook (McGraw-Hill, New York, 1957).

9. Fried, L. E., and Howard, W. M., *J. Chem. Phys.* 109 (17): 7338-7348 (1998).

10. Zaug J. M., Brown J. M., and Slutsky L. J., *J. Phys. Chem.*, 98, 6008-6016, (1994).